

EXHIBIT

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Communications

Opening and Purification of Carbon Nanotubes in High Yields**

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Carbon nanotubes can be thought of as cylindrical graphitic micro-crystals with nanometer diameters which are expected to have unique properties.^[1] Currently multi-shell nanotubes can be made in gram-orders using the carbon arc discharge synthesis method.^[2, 3] However, the crude sample contains not only nanotubes but also nanoparticles with a weight ratio of about 2:1 in the best cases. Therefore the nanotubes must be further purified in order to investigate precisely their properties.

Recently we reported the purification of nanotubes by oxidation in air at high temperature (around 750 °C).^[4] In this process the nanoparticles are consumed more rapidly than the nanotubes. However the yields are very small (< 1%) probably due to the local inhomogeneities in the gas phase oxidation process. To overcome this problem, we have investigated the liquid-phase oxidation of the crude nanotube samples and found that under suitable conditions high yields of opened purified nanotubes can be obtained.

In this paper we describe this method which gives yields of the order of 40% depending on the composition of the crude sample. This method is very useful to obtain gram-quantities of purified nanotubes at one time under well-controlled conditions.

By analogy with the gas-phase oxidation referred to earlier,^[4] we tried several well-known strong oxidants, such as nitric acid, sulfuric acid, the mixture of both and potassium permanganate. Transmission electron microscopy (TEM) observation revealed that the oxidation was much more homogeneous in solution where the nanotube sample could be well dispersed through sonication and the chemical attack could be uniform. The oxidation by sulfuric and nitric acids is extremely slow and weak. A mixture of the two gives slightly better results.

For purification purposes, by far the best oxidant is potassium permanganate in acidic solution. Therefore, for the latter case, the methodology will be described in detail next. 1.00 g of the core fibrous material is taken from the deposit synthesized by the carbon arc discharge method,^[2, 3] ground and dispersed in 200 ml of 1 N sulfuric acid. This solution is placed in a two necked flask fitted with a reflux condenser.

Separately, 19.8 g (1.5 molar excess in terms of atomic carbon content) of potassium permanganate is dissolved in 200 ml of 1N sulfuric acid and placed in a funnel fitted to the side neck of the flask. The flask is heated to 150 °C in an oil bath with vigorous stirring (magnetic stirrer). The potassium permanganate solution is then added drop by drop through the side funnel. The solution is then refluxed for an additional 3 hours. The mixture is then cooled and filtered through a G4 glass filter (pore size 10–16 mm). The filtrate is washed with pure water and then with concentrated hydrochloric acid to remove the manganese(IV) oxide (reduced from the original potassium permanganate). When all the manganese oxide has been dissolved away, the filtrate is again washed with pure water. The residual filtrate containing the purified nanotubes is collected and dried under vacuum for several hours.

The yield of the purified nanotubes is about 40% in terms of the total weight of the starting raw material. Figure 1 shows the TEM pictures of the sample before and after this



Fig. 1. Carbon nanotubes before (a) and after (b) liquid phase purification.

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[**] We thank M. M. J. Treacy and M. E. Bisher for the micro X-ray analysis of the sample. Since submission of this manuscript, a method for opening nanotubes by nitric acid has been reported (Thang et al., *Nature* 1994, 372, 179) and also confirming that nanotubes are wet by low surface tension liquids such as solvents as predicted in [7].

process. As can be seen the nanoparticles have been removed. Sometimes some new impurities appear in the sample due to the numerous steps in the process. Micro X-ray analysis indicates one impurity is composed of silicon. This is most likely due to the etching of the glass flask by the boiling sulfuric acid and potassium permanganate mixture. This should be easily removed by treating the sample with HF, or using a different container. The maximum yield cannot be higher than the amount of nanotubes in the original crude sample. Therefore the necessary excess of potassium permanganate with respect to the starting material must be calibrated to the weight ratio of nanoparticles to nanotubes in the sample.

In our case, TEM observations revealed that when the molar ratio is around 0.2, the nanotubes begin to open and the nanoparticles become round due to reaction at the edges. When the molar ratio is about 1.5, the nanotubes are purified. However if the excess is further increased (e.g. 2.2), the nanotubes become shortened due to the excessive oxidation. The shortening is due to the fact that oxidation starts at the tips of the nanotubes as has been shown elsewhere.^[5,6] This is mostly due to strain at the tip which enhance its reaction rate.^[1]

The purification process therefore also opens the nanotubes on a large scale. This will be useful for doing nanoscale experiments in the hollow cavities of the nanotubes since we have shown elsewhere that they are wettable by low surface tension liquids.^[7] The oxidation process changes the chemical make-up of the reactive edge of the tips and perhaps even the outer (and the inner) layer of the nanotube. This in turn might affect their properties. To check for any significant chemical modification, the purified nanotubes were analyzed by XPS (ESCA). The detailed results of the XPS analysis will be described elsewhere.^[8]

Figure 2 shows the peak-separated difference XPS spectrum of the purified nanotubes around 285 eV. The main

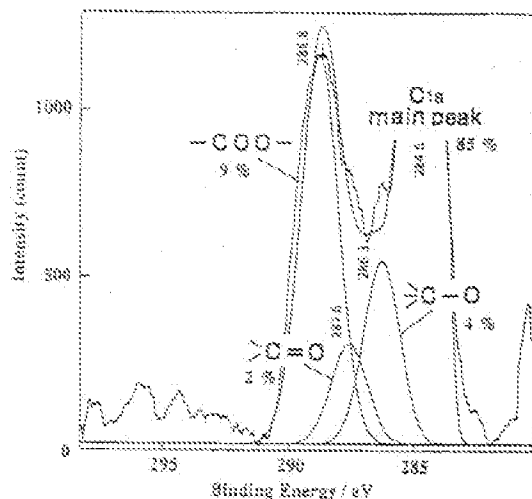


Fig. 2. The peak-separated XPS spectrum of the purified nanotubes around 285 eV. The weight percent of each of the chemical groups present are indicated.

peak (cut off) at 284.6 eV is unambiguously assigned to the C1s of graphitic carbon. The shoulder of the main peak is composed of three peaks, which are assigned to the C1s of hydroxyl carbon (286.3 eV), that of carbonyl carbon (287.6 eV) and that of carboxyl carbon (288.8 eV). The analysis of the peak areas indicates that ca. 15 percent of the carbon constituting the nanotubes are bound to those groups as indicated in Figure 2. Clearly, not only the tips but also the surface of the outer layer is covered with these species. The presence of these hydrophilic group is noticeable in that the purified nanotubes disperse much more easily in water than the original sample.

In conclusion, we have presented a simple method to obtain opened and purified nanotubes in high yields which should allow for their accurate physical characterization. With the resultant higher dispersibility, this method also opens the way for further chemical decoration and modification of carbon nanotubes and their eventual use in biomimetic systems.

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Photoconductivity in the Columnar Phases of a Glassy Discotic Twin**

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The electronic charge-carrier mobilities of organic systems are mainly determined by the supramolecular arrangement and packing of the molecular units involved. The overlap of molecular wavefunctions is often more important than the

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